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A Tetrakisstibine Complex of Platinum(II)

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Although it is thought that stibine ligands should promote pentacoordination for platinum(II) [1], until recently only planar complexes had been isolated in reactions of monodentate tertiary stibines with platinum(II). In a study of the coordination of mixed alkyl–aryl stibines to platinum [2], the pentacoordinate complexes $[Pt(SbPh_2Me)_3I_2]$ and $[Pt(SbPhMe_2)_3I_2]$ have been prepared. It was found that phenyldimethylstibine formed a tetrakis-ligand complex, $[Pt(SbPhMe_2)_4Cl_2]$, which we previously assumed to be four-coordinate. We wish to report a more full investigation of this complex.

Experimental

Physical measurements were obtained as previously described [2]. The complex $[Pt(SbPhMe_2)_4Cl_2]$ was prepared as previously described [2]. *Anal.* Found C, 32.6; H, 3.8; Cl, 5.9. $C_{32}H_{44}Cl_2PtSb_4$ requires C, 32.5; H, 3.8; Cl, 6.0%.

Preparation of $[Pt(SbPhMe_2)_4](ClO_4)_2$

A solution of the complex $[Pt(SbPhMe_2)_2Cl_2]$ (0.72 g, 1 mmol) in dichloromethane (20 cm^3) was stirred with silver(I) perchlorate (0.41 g, 2 mmol) in an inert atmosphere. Acetonitrile (5 cm^3) was added, and the mixture was stirred for 20 minutes. The silver chloride was removed by filtration, and the filtrate was stirred with $PhMe_2Sb$(0.46 g, 2 mmol) for 30 minutes. The solvent was removed by room temperature evaporation and the resulting solid was recrystallised from dichloromethane/ethanol. *Anal.* Found C, 29.3; H, 3.4; Cl, 5.8. $C_{32}H_{44}Cl_2O_8PtSb_4$ requires C, 29.3; H, 3.4; Sl, 5.4%.

Results and Discussion

$[Pt(SbPhMe_2)_4Cl_2]$

No ν(Pt–Cl) absorption band can be seen in the infrared spectrum of the complex $[Pt(SbPhMe_2)_4Cl_2]$, suggesting either that it has an ionic structure in the solid state or that it has a tetragonal structure [3–5] with weakly bound chlorine atoms. In view of its behaviour as a nonconductor in nitromethane solution, it is likely that $[Pt(SbPhMe_2)_4Cl_2]$ is tetragonal. Its reflectance spectrum shows a strong absorption at 24.3kK, strongly indicative of planar coordination as would be expected if there were marked tetragonal distortion in the solid state.

The behaviour of this tetrakis-ligand complex in chloroform and dichloromethane solutions is quite complex. The molecular weight in chloroform is 528 (*cf.* calculated value 1182), suggesting that considerable dissociation takes place in solution. It is unlikely that the complex dissociates by loss of chloride ions, since it is a nonconductor in both nitromethane and 1,2-dichloroethane.

A solution of $[Pt(SbPhMe_2)_4Cl_2]$ in $CDCl_3$ shows a single methyl resonance in the n.m.r. spectrum at 8.89τ. This signal lies almost exactly half way between those of the bis-ligand complex (8.62τ) and free ligand (9.19τ). This could either be coincidental or indicative of a fast exchange reaction between free and coordinated ligand:

$$[Pt(SbPhMe_2)_4Cl_2] \rightleftharpoons [Pt(SbPhMe_2)_2Cl_2] + 2SbPhMe_2$$

Reaction of bis-ligand complex with $SbPhMe_2$ in 1:2 ratio in dichloromethane produces a solution with identical electronic spectrum to that of the tetrakis-ligand complex. If this reaction is carried out in $CDCl_3$, the resulting solution shows a single methyl resonance at 8.89τ (*cf.* a value of 8.96τ calculated on the basis of a fast exchange between free and coordinated ligand).

Attempts to freeze this fast exchange reaction by cooling the $CDCl_3$ solution have proved unsuccessful, there being no change in n.m.r. spectrum on cooling the solution from 34 °C to 70 °C.

$[Pt(SbPhMe_2)_4](ClO_4)_2$

The ionic complex $[Pt(SbPhMe_2)_4](ClO_4)_2$ behaves as a 2:1 electrolyte in $10^{-4}M$ nitromethane solution (Λ_m = 168 cm^2 Ω^{-1} mol^{-1}) and has an electronic spectrum in dichloromethane solution characteristic of planar solution (ϵ_{max} = 32.5kK (sh)). In nitromethane solution, the complex is yellow, *cf.* the colourless dichloromethane solution, and exhibits and absorption at 26.2kK. It seems probable that a molecule of solvent coordinates to the platinum atom giving a pertacoordinate structure.

The conductimetric titration of 2.5 × $10^{-4}M$ solution of $[Pt(SbPhMe_2)_4](ClO_4)_2$ in nitromethane with a 5 × $10^{-3}M$ solution of $[Ph_3PCH_2Cl]^+Cl^-$ shows an end-point after addition of only *one* equivalent of Cl^- – a surprising result in view of the existence of $[Pt(SbPhMe_2)_4Cl_2]$. This solution exhibits an absorption at 26.2kK and the chromophore must presumable also be pentacoordinate. The obvious reaction is the replacement of the solvent molecule by a chlorine atom:

$$Pt(SbPhMe_2)_4(MeNO_2)]^{2+} + Cl^- \longrightarrow$$
$$[Pt(SbPhMe_2)_4Cl]^+ + MeNO_2$$

Addition of further Cl^- has no effect.

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